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Manganese thermite based on blends of MnO and Mn2O3

Making manganese metal by thermite reduction of manganese oxides is one of the more frustrating oxide reductions I've ever carried out.

To get a better understanding of what the issues are I'd firstly recommended reading my blog post on this subject.

The issue with manganese thermite, especially from the higher oxides $MnO_2$and Mn_3O_4, is that these reactions generate so much heat that in adiabatic conditions the temperature of the reaction products will exceed the boiling point (BP) of Mn (2,061 C, 2,334 K). It's this characteristic that causes MnO_2 thermites to deflagrate often violently, almost 'explosively'. The end-temperature of a thermite reaction (in adiabatic conditions) can be estimated quite accurately from the molar reaction heat (ΔH, reaction enthalpy), and the molar heat capacities and molar heats of fusion of the reaction products, basically by applying Hess's Law. If of interest to readers I can give an example of such a calculation (on request).

The obvious solution to the problem would be to create conditions in which the reaction enthalpy is either lower or partly dissipates away (non-adiabatic conditions) but there's another problem complicating this approach.

For a thermite reaction to yield liquid metal, separated from the liquid slag (both solidify on cooling of course), the melting point (MP) of both (whichever is highest) the produced metal and the by-product alumina (Al_2O_3) has to be reached at the end of the reaction. For alumina the MP is 2,327 K (2,054 C), for Mn, 1,519 K. But as stated before, the BP of Mn is also only 2,061 C, perilously close to the MP of alumina.

This creates a real lose-lose situation: to achieve metal-slag separation of Mn/Al_2O_3 this mixture has to reach a temperature that's really close to the BP of manganese metal. Even higher temperatures will cause much of the Mn metal to simply boil off. At temperatures somewhat below the MP of alumina, the vapour pressure of the Mn will be less but metal/slag separation will not be able to occur, resulting in powdered, sintered metal frozen in the slag.

Accurate control of the end-temperature in near-adiabatic conditions is thus essential to obtain any *lump* metal from such a reduction.

I therefore started out on a series of experiments designed to cool the MnO_2 thermite by co-reducing MnO_2 and MnO. The reaction enthalpies per mol of oxide for both reductions are respectively - 597 kJ per mol of $MnO_2$and - 173 kJ per mol of MnO. Initial results with a blend of 1 mol MnO and 0.4 mol MnO_2 and a high level of CaF_2 (calcium fluoride, fluorite, fluorspar) as a heat sink and slag fluidiser, showed that this kind of mix with a stoichiometric amount of Al powder is capable of making nice blobs of clean Mn metal, albeit at low yields.

In the mean time I've switched from MnO_2 to Mn_2O_3 because thermochemical calculations show that an Mn_2O_3 runs a *little* cooler than the corresponding MnO_2 reaction, mainly because the Mn_2O_3 reaction generates more moles of reaction products (per mol of Mn_2O_3, 2 mol of Mn and 1 mol Al_2O_3, against 1 mol Mn and 2/3 mol Al_2O_3 for MnO_2).

I've run several small (20 g and 50 g batches) thermites using blends of Mn_2O_3 and MnO, always using a high level of CaF_2. I set the level of CaF_2as a constant molar ratio of CaF_2/Al = 0.225, the alumina slag therefore contains always the same molar fraction of CaF_2.

On the whole the results indicate that obtaining yields (recovered metal/metal present in the oxide x 100 %) is hard to push much beyond 35 % or so. The last two batches, both with 50 g stoichiometric (and CaF_2 = 0.225 molar ratio) mixes, gave the following yields:

.....mol.....mol

Mn_2O_3.....1.....1
MnO.....1.....0

Yield.....37 %.....19 %

The 1/0.5 blend gave the highest yield of Mn metal I've ever achieved (out of probably over 20 or so reactions) and the metal is clean skinned and solid. The largest regulus was 7.3 g. Both reactions ran well-contained, leaving a molten slag/metal puddle at the bottom of the crucible. The 1/0 batch yielded metal that was significantly more oxidised, yet on the whole of passable quality.

It's clear though although these results constitute a great improvement to the usual 'explosive' MnO_2 thermite, there is only so much cooling the Mn_2O_3 thermite by blending it with the much cooler MnO can actually achieve in terms of yield improvement.

The only real solution to reducing Mn oxides (or halides) with higher yields is by using a reductant with a much lower melting oxide (or halide).

One such reaction that springs to mind is the reduction of anhydrous $MnCl_2$with Mg. The reaction enthalpy of $MnCl_2$ + Mg ---> Mn + $MgCl_2$ is unfortunately only a measly - 161 kJ/mol of $MnCl_2$, about a 100 kJ short of success. Thermocalcs show that in adiabatic conditions the reaction products would be heated to about 1,200 K, well above the MP of $MgCl_2$(987 K) but about 300 K short of the MP of Mn (1,519 K). Pre-heating the mixture by about 300 K or simply heating it to spontaneous ignition could work to obtain liquid Mn and liquid $MgCl_2$. It *may* also be possible to use the reaction Mg + I_2 ---> MgI_2 (ΔH = - 367 kJ/mol) as a heat-booster system, by adding extra magnesium and iodine to the reagent mix.

As regards using a reductant with an oxide of lower MP, that excludes both Mg and Ca, as both have oxides with insanely high MPs. That then really only leaves the alkali metals, in particular Li and Na.

Thermochemical calculation for the reaction Mn_2O_3 + 6 Li ---> 2 Mn + 3 Li_2O (ΔH = - 838 kJ per mol Mn_2O_3) shows that in adiabatic conditions the estimated end-temperature would be 2,320 K which is still too high and too close to the BP of Mn.

But here we could blend with MnO again. Setting a target end-temperature of 2,000 K (well above the MP of Mn, yet well below its BP as well), the blend composition of a stoichiometric mix has been estimated to be about 1 mol Mn_2O_3 + 2.6 mol MnO.

One small problem: *I haven't got any Li...*

Sodium, with a ΔH = - 295 kJ per mol Mn_2O_3 for Mn_2O_3 + 6 Na ---> 2 Mn + 3 Na_2O could also be a good candidate... *Haven't got any Na either...*